

**FINAL VERSION**

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**Title:** Isocyanate-Based Polymer Foam and Process for Production Thereof

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[illegible]



**D E F O R M A T I O N**

[0008] Accordingly, it would be desirable to have an isocyanate-based foam, preferably a polyurethane foam which is a low resilient foam and which has an energy dissipation profile substantially unaffected over a relatively wide temperature range.

[0009] It is an object of the present invention to provide a novel isocyanate based foam which obviates or mitigates at least one of the above-mentioned disadvantages of the prior art.

**[0011]** Accordingly, in one of its aspects, the present invention provides a flexible isocyanate-based polymeric foam which has:

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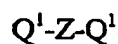




[0021] The selection of an isocyanate suitable for use in the reaction mixture is within the purview of a person skilled in the art. Generally, the isocyanate compound suitable for use may be represented by the general formula:



wherein  $i$  is an integer of two or more and  $Q$  is an organic radical having the valence of  $i$ .  $Q$  may be a substituted or unsubstituted hydrocarbon group (e.g., an alkylene or arylene group). Moreover,  $Q$  may be represented by the general formula:



wherein  $Q^1$  is an alkylene or arylene group and  $Z$  is chosen from the group comprising  $-O-$ ,  $-O-Q^1-$ ,  $-CO-$ ,  $-S-$ ,  $-S-Q^1-S-$  and  $-SO_2-$ . Examples of isocyanate compounds which fall within the scope of this definition include hexamethylene diisocyanate, 1,8-diisocyanato-*p*-methane, xylyl diisocyanate,  $(OCNCH_2CH_2CH_2OCH_2O)_2$ , 1-methyl-2,4-diisocyanatocyclohexane, phenylene diisocyanates, tolylene diisocyanates, chlorophenylene diisocyanates, diphenylmethane-4,4'-diisocyanate, naphthalene-1,5-diisocyanate, triphenylmethane-4,4',4"-triisocyanate and isopropylbenzene- $\alpha$ -4-diisocyanate.

[0022] In another embodiment,  $Q$  may also represent a polyurethane radical having a valence of  $i$ . In this case  $Q(NCO)_i$  is a compound which is commonly referred to in the art as a prepolymer. Generally, a prepolymer may be prepared by reacting a stoichiometric excess of an isocyanate compound (as defined hereinabove) with an active hydrogen-containing compound (as defined hereinafter), preferably the polyhydroxyl-containing materials or polyols described below. In this embodiment, the polyisocyanate may be, for example, used in proportions of from about 30 percent to about 200 percent stoichiometric excess with respect to the proportion of hydroxyl in the polyol. Since the process of the present invention may relate to the production of polyurea foams, it will be appreciated that

[illegible]

**[0023]** In another embodiment, the isocyanate compound suitable for use in the process of the present invention may be selected from dimers and trimers of isocyanates and diisocyanates, and from polymeric diisocyanates having the general formula:



wherein both i and j are integers having a value of 2 or more, and Q" is a polyfunctional organic radical, and/or, as additional components in the reaction mixture, compounds having the general formula:



wherein i is an integer having a value of 1 or more and L is a monofunctional or polyfunctional atom or radical. Examples of isocyanate compounds which fall with the scope of this definition include ethylphosphonic diisocyanate, phenylphosphonic diisocyanate, compounds which contain a =Si-NCO group, isocyanate compounds derived from sulphonamides (QSO<sub>2</sub>NCO), cyanic acid and thiocyanic acid.

**[0024]** See also for example, British patent number 1,453,258, for a discussion of suitable isocyanates.

**[0025]** Non-limiting examples of suitable isocyanates include: 1,6-hexamethylene diisocyanate, 1,4-butylene diisocyanate, furfurylidene diisocyanate, 2,4-toluene diisocyanate, 2,6-toluene diisocyanate, 2,4'-diphenylmethane diisocyanate, 4,4'-diphenylmethane diisocyanate, 4,4'-diphenylpropane diisocyanate, 4,4'-diphenyl-3,3'-dimethyl methane diisocyanate, 1,5-naphthalene diisocyanate, 1-methyl-2,4-diisocyanate-5-chlorobenzene, 2,4-diisocyanato-s-triazine, 1-methyl-2,4-diisocyanato cyclohexane, p-phenylene diisocyanate, m-phenylene diisocyanate, 1,4-naphthalene diisocyanate, dianisidine diisocyanate, bitolylene diisocyanate, 1,4-xylylene diisocyanate, 1,3-xylylene diisocyanate, bis-(4-

isocyanatophenyl)methane, bis-(3-methyl-4-isocyanatophenyl)methane, polymethylene polyphenyl polyisocyanates and mixtures thereof.

[0026] A more preferred isocyanate is selected from the group comprising 2,4-toluene diisocyanate, 2,6-toluene diisocyanate and mixtures thereof, for example, a mixture comprising from about 75 to about 85 percent by weight 2,4-toluene diisocyanate and from about 15 to about 25 percent by weight 2,6-toluene diisocyanate.

[0027] Another more preferred isocyanate is selected from the group comprising 2,4'-diphenylmethane diisocyanate, 4,4'-diphenylmethane diisocyanate, modified 4,4'-diphenylmethane diisocyanate (modified to liquefy the diisocyanate at ambient temperature) and mixtures thereof.

[0028] The most preferred isocyanate is a mixture comprising (i) a prepolymer of 4,4'-diphenylmethane diisocyanate and (ii) a carbodiimide-derivative based on 4,4'-diphenylmethane diisocyanate. Preferably the mixture comprises a weight ratio of (i):(ii) in the range of from about 1:1 to about 9:1.

[0029] Preferably, the isocyanate used in the present process has a functionality in the range of from about 2.0 to about 2.7, more preferably in the range of from about 2.0 to about 2.3.

[0030] The isocyanate preferably is used in an amount to provide an isocyanate index, inclusive of all reactive equivalents in the reaction mixture, in the range of from about 60 to about 110, more preferably from about 70 to about 100, most preferably from about 80 to about 90.

[0031] If the process is utilized to produce a polyurethane foam, the active hydrogen-containing compound is typically a polyol.

[0032] The choice of polyol suitable for use herein is within the purview of a person skilled in the art. For example, the polyol may be a hydroxyl-terminated backbone of a member selected from the group comprising polyether, polyester, polycarbonate, polydiene and polycaprolactone. Preferably, the polyol is selected from the group comprising hydroxyl-terminated polyhydrocarbons, hydroxyl-terminated polyformals, fatty acid triglycerides, hydroxyl-terminated polyesters, hydroxymethyl-terminated polyesters,







water used in the production of a foamed isocyanate-based polymer typically is limited by the fixed properties expected in the foamed polymer and by the tolerance of the expanding foam towards self structure formation.

[0039] The reaction mixture used to produce the present foamed isocyanate-based polymer typically will further comprise a catalyst. The catalyst used in the reaction mixture is a compound capable of catalyzing the polymerization reaction. Such catalysts are known, and the choice and concentration thereof in the reaction mixture is within the purview of a person skilled in the art. See, for example, United States patents 4,296,213 and 4,518,778 for a discussion of suitable catalyst compounds. Non-limiting examples of suitable catalysts include tertiary amines and/or organometallic compounds. It is also possible to utilize the so-called delayed action catalysts. Of course it will be understood by those skilled in the art that a combination of two or more catalysts may be suitably used.

[0040] The plasticizer used in the present process a plasticizer is selected from the group comprising: a halogenated paraffin, a  $C_2/C_4$  aliphatic polymer comprising a primary hydroxyl group, and mixtures thereof.

[0041] Preferably the plasticizer is used in an amount of less than about 20 parts by weight, more preferably from about 2 to about 15 parts by weight, most preferably from about 6 to about 10 parts by weight, per hundred parts by weight active hydrogen-containing compound used in the reaction mixture.

[0042] Preferably, the halogenated paraffin comprises a chlorinated paraffin. More preferably, the halogenated paraffin has a molecular weight in the range of from about 300 to about 800, preferably from about 400 to about 700, most preferably from about 500 to about 550. Preferably, the halogenated paraffin has a density in the range of from about 1.0 to about 1.5 g/mL, more preferably from about 1.2 to about 1.4 g/mL. Preferably, the halogenated paraffin has a viscosity at 25°C of from about 5.0 to about 15 Pa·s, more preferably from about 8.0 to about 12 Pa·s. A non-limiting example of a halogenated paraffin having many of the preferred features is commercially available from Pioneer under the tradename Cereclor™ S-56.



FLEXIBLE FOAM FUNDAMENTALS, Herrington et al. (1991) and the references cited therein.

[0046] The manner by which the polyol mixture, isocyanate, blowing agent, particulate material and catalyst are contacted in the first step of the present process is not particularly restricted. Thus, it is possible to preblend the components in a separate tank which is then connected to a suitable mixing device for mixing with the blowing agent and catalyst. Alternatively, it is possible to preblend the active hydrogen-containing compound with the blowing agent, catalyst and other additives, if present, to form a resin. This resin preblend could then be fed to a suitable mixhead (high pressure or low pressure) which would also receive an independent stream of the isocyanate.

[0047] Once the active hydrogen-containing compound, isocyanate, blowing agent, chain extending agent and catalyst have been contacted and, ideally, mixed uniformly, a reaction mixture is formed. This reaction mixture is then expanded to produce the present isocyanate-based polyurethane foam. As will be apparent to those of skill in the art, the process of the present invention is useful in the production of slabstock foam, molded articles and the like. The manner by which expansion of the reaction mixture is effected will be dictated by the type of foam being produced.

[0048] Embodiments of the present invention will now be described with reference to the following Examples which should not be construed as limiting the scope of the invention. The term "pbw" used in the Examples refers to parts by weight.

[0049] In the Examples, the following materials were used:

Voranol™ V4815, a polyol commercially available from The Dow Chemical Company;

Poly G20-112, a polyol commercially available from Arch. Chemicals;

Poly G20-56, a polyol commercially available from Arch. Chemicals;

E850, a 43% solids content copolymer (SAN) polyol, commercially available from Bayer Corporation;

Isonate™ 143L, an isocyanate, commercially available from The Dow Chemical Company;

Rubinate™ 7302, an isocyanate, commercially available from Huntsman Chemicals;

DPG, dipropyleneglycol, a cross-linking agent;

DEOA-LF, diethanolamine, a cross-linking agent commercially available from Air Products;

Water, an indirect blowing agent;

Kraton™ L-1203, a plasticizer, commercially available from Shell;

Dabco™ 33LV, a gelation catalyst, commercially available from Air Products;

Niax™ A-1, a blowing catalyst, commercially available from Witco;

V-4053, a cell opener, commercially available from Dow Chemical Company;

DC-5169, a surfactant, commercially available from Air Products;

NP-50, a catalyst, commercially available from Huntsman Chemicals;

B-4113, a surfactant, commercially available from Goldschmidt;

B-8240, a surfactant, commercially available from Goldschmidt;

B-4690, a surfactant, commercially available from Goldschmidt

T-12, organometallic catalyst, commercially available from Air Products; and

Cereclor™ S-56, a plasticizer commercially available from Pioneer.

#### Examples 1-5

[0050] In these Examples, a series of polyurethane foams were produced using the formulations set forth in Table 1.

[0051] The general procedure used to produce the foam in the Examples was as follows.

[0052] In the Examples, the foam was produced using a machine pouring technique. Thus, in this technique, a resin blend was created in a drum by adding to the drum the specific amounts (see Table 1) of the following ingredients in the order listed: base polyol,

surfactant(s), extender(s)/cross-linker(s), catalyst(s) and other additive(s). The resulting resin blend was mixed for 60 minutes using an air driven mixer at 300-500 rpm at 23°C. The resin blend, together with isocyanate(s), was immediately loaded into a Cannon™ H40/2S high pressure impingement mixing foam dispenser equipped with an HPL-18 mixing head. The foamable composition was mixed at 2000-3000 psi and then poured into the mold. The foamable composition was dispensed in a 10" x 10" x 4" aluminum mold heated to 65°C. The foam was demolded after 6 minutes and left to cool down to 23°C and ~50% relative humidity where it was kept at these conditions for 7 days prior to testing.

[0053] The resultant foams were subjected to various tests. The results of these tests are reported in Table 2.

[0054] In Table 2, the glass transition temperature ( $T_g$ ) was determined by Dynamic Mechanical Thermal Analysis (DMTA) in accordance with ASTM D4065-93, adapted to measure  $T_g$  at the onset of the drop in the elastic modulus. The equipment used for the test was obtained from Rheometric Scientific (Model DMTA IV). The following test conditions were employed:

Sample size:	Length 7 mm
	Diameter 16 mm
Test type:	Dynamic Temperature Ramp
Mode:	Compression
Initial temperature:	-75°C
Final temperature:	+150°C
Ramp rate:	3.5°C/minute
Frequency:	1 Hz
Strain:	0.1%
Cooling agent:	Liquid nitrogen

During the course of the test, the stored modulus ( $E'$ ) (or stored elastic energy) for each sample was routinely recorded. The loss modulus ( $E''$ ) (or viscous energy dissipation) and

the ratio of loss modulus to stored modulus ( $E''/E'$ ), also known as  $\tan \delta$ , were calculated and are reported in Table 2. As is known in the art,  $\tan \delta$  may be used to infer the amount of energy dissipated as heat during deformation of the foam. It is highly desirable to have a foam with a  $\tan \delta$  that does not vary greatly over as wide a temperature range as possible. This is particularly so when the foam is being used in an energy management capacity such as a vehicular trim element where the vehicle may be in service over a wide range of temperatures.

[0055] With further reference to Table 2, the ball rebound property of each foam sample was determined using ASTM D-3574H as an average of three measurements taken in three different locations of the test sample. The equipment used was a Ball Rebound Tester (Model TT502), commercially available from Time Tech.

[0056] With further reference to Table 2, the compression set at 50% deflection of each foam sample was determined using ASTM D-3574 (Test D).

[0057] The results reported in Table 2 and illustrated in Figure 1 clearly illustrate the superiority of the foam samples produced in Examples 1-5.

[0058] As will be appreciated by those of skill in the art, the "viscoelasticity" of the foam samples is assessed by measuring the ball rebound property of each foam sample. Further, energy dissipation is assessed by measuring impact. Still further the low temperature behaviour and predictability of other physical properties is assessed by measuring  $T_g$  and  $\tan \delta$ , respectively, of each foam sample. Finally, the elastic property was assessed by measuring compression set (CS) at 50% deflection of each foam sample.

[0059] With particular reference to Figure 1, it will be seen that the  $\tan \delta$  value for each foam is relative unchanged - i.e., the curve is relatively flat - over a broad temperature range (e.g.,  $-30^\circ\text{C}$  to  $+105^\circ\text{C}$ ). Thus, the polymer in foam can be said to have a substantially predictable and constant response to an applied load over a broad temperature. With reference to Table 2, the relatively low  $T_g$  values of the foams of Examples 1-5 illustrate that the polymer remains relatively soft at low temperatures. The ball rebound results illustrate that the foams of Examples 1-5 have low resiliency (i.e., ball rebound less than about 30%).







[illegible]

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TABLE 2

Example	Tg (°C)	Tan δ: Measured Tg to +60°C					BR <sup>2</sup> (%)	CS <sup>3</sup> (%)
		Min.	Max	Median	Var. <sup>1</sup> (%)			
1	-31	0.26	0.32	0.29	10.3		19	88
2	-35	0.20	0.30	0.25	20.0		19	89
3	-28	0.26	0.39	0.325	20.0		16	90
4	-25	0.22	0.39	0.305	27.9		23	37
5	-31	0.21	0.37	0.29	27.6		26	55

<sup>1</sup>Var. = maximum variance (+ or -) from median value of Tan δ

<sup>2</sup>BR = ball rebound

<sup>3</sup>CS = compression set at 50% deflection

**TABLE 3**

Sample	Change in Ball Rebound Property (%)
Example 1	-14
Example 3	-14
VEF-1	+140
VEF-2	+100
VEF-3	+800

**TABLE 4**

Sample	Ball Rebound @ 23°C (%)	Ball Rebound @ 80°C (%)
Example 1	19	21
Example 3	16	22
VEF-1	5	31
VEF-3	1	13